Nematic-Isotropic Transition in Porous Media

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Motivated by recent experiments on the nematic-isotropic transition in porous media, two simplified models are proposed and studied using mean field theory and Monte Carlo simulations. The results are in qualitative accord with those found in the experiments.

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Recently, the nematic ordering of liquid crystals contained within a porous medium has been studied using light scattering and calorimetry measurements [1,2]. These experiments indicate that the first order transition in the absence of the confining porous medium is replaced by a smooth evolution to a glassy state in which the correlation length does not exceed the characteristic pore size. Even though the relaxation time was found to become very large compared to experimentally accessible times, no hysteresis was observed. Here, we study this problem theoretically—a range of models is considered and studied using mean field theory enabling the determination of the simplest model that captures the physics of the liquid crystal system. Our mean field studies are complemented by Monte Carlo simulations in three dimensions in order to eliminate certain spurious features of the mean field analysis, to assess the effect of fluctuations, and to study the dynamics. Taken together, mean field theory and computer simulations for the model system yield results in good accord with experiment.

We associate the effects of the porous medium with that of a random field [3]. Unlike conventional spins, the director of a liquid crystal is a headless vector [1]—the spin may be thought of as a rod with its orientation being specified in a half sphere of orientational space.

We propose the Hamiltonian

$$H = H_0 + H_1 = -J\sum_{\langle ij\rangle}(\mathbf{S}_i\cdot\mathbf{S}_j)^2 - \sum_i \mathbf{h}_i\cdot\mathbf{S}_i\,, \quad (1)$$

where $\mathbf{S}_i$ is a n-component unit vector (in the liquid crystal context $n = 3$) and the h_i's are independently chosen quenched fields distributed according to a probability density $P(|\mathbf{h}|)$ which is rotationally invariant. The Hamiltonian H_0 is variously called the Lebwohl-Lasher model [4], the Maier-Saupe model [5] (in the context of liquid crystals), and the RP^{n-1} model [6] (in field theory) [7]. The free energy of a generalized version of the Hamiltonian in (1)

$$H' = -J\sum_{\langle i,j\rangle}(\mathbf{S}_i\cdot\mathbf{S}_j)^2 - \sum_i \varepsilon_i\mathbf{h}_i\cdot\mathbf{S}_i\,, \quad (2)$$

where the ε_i are site variables that take on values $+1$ or -1, is identical to the free energy of (1) for any arbitrary set of $\{\varepsilon_i\}$. This follows from the local gauge invariance of H_0. In other words, redefining $\varepsilon_i\mathbf{s}_i = \mathbf{t}_i$, and noting that the trace over the $\mathbf{s}_i$ variables is equivalent to the trace over the $\mathbf{t}_i$ variables and $\varepsilon_i^2 = 1$, the free energy is the same for each of the 2^N sets of choices of $\{\varepsilon_i\}$ (N, here, denotes the number of sites). We exploit this equality by tracing over the ε_i variables (since each of the 2^N partition functions are exactly equal, the individual partition function is $\frac{1}{2}N$ of this trace—this results in a trivial contribution to the entropy) to show that our coupling H_1 is exactly equivalent to $\sum_i \ln\cosh(\beta\mathbf{s}_i\cdot\mathbf{h}_i)$ which is a special case of the generic form proposed by Gingras [8] of $\sum_m\sum_i a_m(\mathbf{h}_i\cdot\mathbf{S}_i)^{2m}$. Thus, even though our Hamiltonian (1) has an external field term coupled linearly to the director, the symmetries of H_0 make it exactly equivalent to biquadratic and higher order even couplings. (Note that this result obtains for any realization of the disorder in $\mathbf{h}_i$.)

We will begin with the infinite range version of (1),

$$H = -\frac{J}{2N}\sum_{i,j}(\mathbf{S}_i\cdot\mathbf{S}_j)^2 - \sum_i \mathbf{h}_i\cdot\mathbf{S}_i\,. \quad (3)$$

Generalizing the method of Schneider and Pytte [9], one may rigorously prove that the free energy of (3) is given by the minimum of

$$F = \mathrm{tr}x^2 + \frac{1}{\beta}\langle V(x,h)\rangle_h + (\text{irrelevant constant}), \quad (4)$$

where $x = (x_{\alpha\beta})$ is a symmetric, traceless $n\times n$ matrix, whose equilibrium value is

$$\left\langle \frac{ns^\alpha s^\beta - \delta^{\alpha\beta}}{n-1}\right\rangle,$$

$$e^{-V(x,h)} = \int d^{n-1}\hat{\mathbf{s}}\,\exp\left\{\beta\left(2\sum_{\alpha\beta}x_{\alpha\beta}\frac{ns^\alpha s^\beta - \delta^{\alpha\beta}}{n-1} + \mathbf{h}\cdot\mathbf{s}\right)\right\}, \quad (5)$$

and

$$\langle V(x,h)\rangle_h = \int d^n h\, P(h)V(x,h)\,. \quad (6)$$

We will choose to measure $1/\beta$ and h in units of J.

We now specialize to the case where only a fraction p of the sites have field $\mathbf{h} = h_0\hat{\mathbf{h}}$, i.e.,

$$P(h) = (1 - p)\delta^n(h) + p\delta(h - h_0)C \tag{7}$$

with $C^{-1} = h_0^{n-1}S_n$, where S_n is the surface area of a unit sphere in n-dimensional space. This choice corresponds to the field being imposed on a fraction p of the sites—the strength of the field is h_0, but its orientation is random. With this choice (5) yields on further specializing to $h_0 \to \infty$

$$V(x,h) = -\frac{2\beta n}{n-1}\sum_{\alpha\beta} x_{\alpha\beta}h^\alpha h^\beta + (x \text{ independent terms}). \tag{8}$$

(The conclusions of this paper are independent of whether the interaction with the external field is of the biquadratic form or of the form $\mathbf{S}_i \cdot \mathbf{h}_i$ as long as $h_0 \to \infty$. The linear coupling is much easier to handle within mean field theory.)

On taking the quenched average (6) and noting that $\mathrm{tr}x = 0$, one finds the simple result

$$F(\beta, 1-p, x) = \mathrm{tr}x^2 - \frac{1-p}{\beta} < \ln \int d^{n-1}\hat{\mathbf{s}} \exp\left\{2\beta \sum_{\alpha\beta} x_{\alpha\beta}\frac{ns^\alpha s^\beta - \delta^{\alpha\beta}}{n-1}\right\}$$

$$\equiv (1-p)^2 F(\beta(1-p), 1, x/(1-p)), \tag{9}$$

where $F(\beta, 1, M)$ is the free energy of the pure system ($p = 0$). In this case, since M (or x) is symmetric, it can be diagonalized. If $\hat{\boldsymbol{l}}$ is the axis of preferred orientation, then

$$ptM_{\alpha\beta} = \left\langle \frac{ns^\alpha s^\beta - \delta^{\alpha\beta}}{n-1} \right\rangle = \delta_{\alpha\beta}m_\alpha \tag{10}$$

with

$$m_\alpha = Q \quad \text{for } \alpha = 1 \quad \text{and } m_\alpha = -\frac{Q}{n-1} \quad \text{for } \alpha > 1. \tag{11}$$

The choice (11) ensures that the matrix $M_{\alpha\beta}$ is traceless. For the pure system, it is well known that a first order transition occurs at $\beta_c(p = 0)$. This follows from the expansion of the free energy in powers of Q of the form $AQ^2 + BQ^3 + CQ^4 + \cdots$. Since symmetry considerations do not dictate that $B \equiv 0$, the Landau criterion indicates a first order transition. Thus, for our case, with $h_0 \to \infty$, and $p \neq 0$,

$$\beta_c^{-1}(p) = \beta_c^{-1}(0)(1 - p) \tag{12}$$

and

$$Q(\beta, 1-p) = (1-p)Q((1-p)\beta, 1). \tag{13}$$

It is immediately clear, physically, that relaxing the condition $h_0 \to \infty$ will only raise the transition temperature, but still lead to a first order phase transition at nonzero temperature for all $p \neq 1$. In the limit of infinite range exchange, the depressed transition temperature compared to the pure system may be readily understood in terms of a fraction $(1 - p)$ of the spins coupled ferromagnetically to each other with the effect of the spins with the $h_0 \to \infty$ field canceling out in the thermodynamic limit—one merely has the effect of dilution.

We now switch to a n-state Potts model in a random field described by the Hamiltonian

$$H = -J\sum_{\langle ij\rangle} \mathbf{s}_i \cdot \mathbf{s}_j - h_0 \sum_i \mathbf{s}_i \cdot \mathbf{h}_i, \tag{14}$$

where the $\mathbf{s}_i$ and $\mathbf{h}_i$ are one among the vectors $\boldsymbol{\sigma}_1, \ldots, \boldsymbol{\sigma}_n$ with

$$\boldsymbol{\sigma}_\alpha \cdot \boldsymbol{\sigma}_\beta = \frac{n\delta_{\alpha\beta} - 1}{n-1} = \begin{cases} 1, & \alpha = \beta, \\ -\dfrac{1}{n-1}, & \alpha \neq \beta. \end{cases} \tag{15}$$

The σ's point from the center to the vertices of a "tetrahadron" in $n - 1$ dimensions. The random field distribution is

$$P(\mathbf{h}_i) = (1-p)\delta(\mathbf{h}_i) + \frac{p}{n}\sum_\alpha \delta(\mathbf{h}_i - \boldsymbol{\sigma}_\alpha). \tag{16}$$

Since

$$\mathbf{s}_i \cdot \mathbf{s}_j = \frac{n\delta_{\mathbf{s}_i,\mathbf{s}_j} - 1}{n-1}, \tag{17}$$

the model (14) is similar to (1), except that the possible directions of the molecular orientation is "quantized." We alert the reader that the symmetry of the ordered phase and the universality class of (1) and (14) are different. Nevertheless, we will show that, within the mean field approximation, an equation identical in form to Eq. (9) is obtained for the simpler Potts model. The analog of the order parameter (10) is

$$\langle \mathbf{s}_i \cdot \boldsymbol{\sigma}_\alpha \rangle = \frac{\langle n\delta_{\mathbf{s}_i,\boldsymbol{\sigma}_\alpha} - 1\rangle}{n-1} = m_\alpha \quad \text{with } \sum_\alpha m_\alpha = 0. \tag{18}$$

The infinite range version of the Potts model is obtained on substituting the first term in (14) with

$$(J/2N)\sum_{ij} \mathbf{s}_i \cdot \mathbf{s}_j. \tag{19}$$

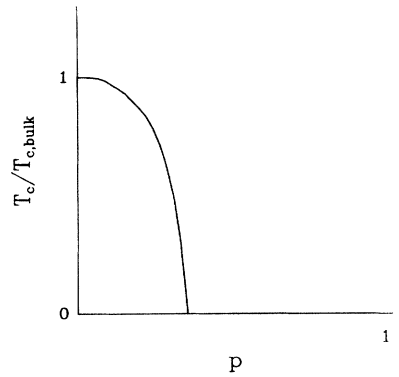

FIG. 1. Schematic plot of the transition temperature normalized to the bulk transition temperature versus p, the concentration of sites with random, infinite field. In the mean field limit, the transition temperature would be zero at $p \equiv 1$.

Proceeding as before, on making the ansatz (11), with $J = 1$, one finds the analogous equation of (14)

$$F(Q) = \frac{1}{2}\left(\frac{n-1}{n}\right)^2 Q^2 - \frac{1}{\beta} V(Q, h_0), \tag{20}$$

with

$$V(Q, h_0) = (1-p)\ln[e^{\beta Q} + (n-1)e^{-\beta Q/(n-1)}] + \frac{p}{n}\sum_{\alpha=1}^{n} \ln\{e^{\beta(Q+h_0\delta_{\alpha,1})} + e^{-\beta Q/(n-1)}[n - 1 + (1-\delta_{\alpha 1})(e^{\beta h_0} - 1)]\}. \tag{21}$$

In the limit $h_0 \to \infty$

$$\lim_{h_0\to\infty} V(Q, h_0) = (1-p)\ln[e^{\beta Q} + (n-1)e^{-\beta Q/(n-1)}] \tag{22}$$

and thus

$$\lim_{h_0\to\infty} F(\beta, 1-p, Q) = \left(\frac{n-1}{n}\right)^2 \frac{Q^2}{2} - \frac{1-p}{\beta}\ln[e^{\beta Q} + (n-1)e^{-\beta Q/(n-1)}] + \text{const} \equiv (1-p)^2 F(\beta(1-p), 1, Q/(1-p)), \tag{23}$$

which is identical to (9). Thus the same conclusions apply here too.

The infinite range model does not incorporate fluctuations, nor does it yield a percolation threshold. It is physically clear that when $p > 1 - p_c$, where p_c is the percolation threshold, the connectivity between the remaining spins (with no field) is no longer present and thus is unable to sustain a nonzero temperature transition. In order to assess the importance of fluctuations, a finite range interaction and a nontrivial percolation threshold and to monitor the short time dynamics, we have undertaken Monte Carlo simulations of the three state Potts model on a cubic lattice with a fraction p of the sites under the influence of an infinitely strong random field favoring one of the three states randomly. Note that our simulations have been carried out for the simple discrete Potts model and *not* for the Hamiltonian (1). While our results are qualitatively consistent with experiments, a direct study of model (1) or the Lebwohl-Lasher model with a biquadratic coupling to the field would be very useful. The Hamiltonian of the model is

$$H = -\sum_{\langle ij\rangle} \delta_{\tilde{t}_i,\tilde{t}_j} \tag{24}$$

with the constraint that a fraction p of the sites have spins *frozen* randomly into one of the three states. The spins $\tilde{t}_i$ take on one of three values a, b, or c. Equation (24) is the same as Eq. (14) with $h_0 \to \infty$ and an exchange interaction equal to $(n-1)/n$. In (24), we have set the exchange equal to 1 and in the figures, the temperature is measured in units of this exchange. Single spin flip dynamics with the standard Glauber scheme were used. It is important to note that the three state Potts model in the pure limit undergoes a first order transition in three dimensions [10]. We define the magnetization, coinciding with the definition (18) and the ansatz (11) as

$$M = \left(\frac{3}{2N\tau}\right)\left[\text{Max}\left\{\sum_{i,t}\delta_{\tilde{t}_i,a}, \sum_{i,t}\delta_{\tilde{t}_i,b}, \sum_{i,t}\delta_{\tilde{t}_i,c}\right\}\right] - 1/2 \tag{25}$$

and the maximum occupation probability (MOP) as

$$P_{\max}^{\text{occ}} = \left(\frac{3}{2N\tau}\right)\left[\sum_{i}\text{Max}\left\{\sum_{t}\delta_{\tilde{t}_i,a}, \sum_{t}\delta_{\tilde{t}_i,b}, \sum_{t}\delta_{\tilde{t}_i,c}\right\}\right] - 1/2, \tag{26}$$

where N is the total number of unfrozen spins, $\tilde{t}_i$ is a function of time, τ is the total time, and the sum over i is over the unfrozen spins. The equilibrium spin-spin correlation function (SSCF) defined as

$$\left(\frac{3}{2N}\right)\sum_i \delta_{\tilde{t}_i(0),\tilde{t}_i(\tau)} - \frac{1}{2}$$

starts with a value of 1 at $\tau = 0$ and quickly (within ~100 passes) drops to a plateau (SSCFP) around which it fluctuates mildly.

Our results are presented in Figs. 1–5. Figure 1 shows a schematic phase diagram deduced from the simulations. Unlike the mean field prediction that the transition temperature goes to zero at $p_{\text{th}} = 1$, the Monte Carlo results yield a value of $p_{\text{th}} < 1 - p_c$ at which the transition

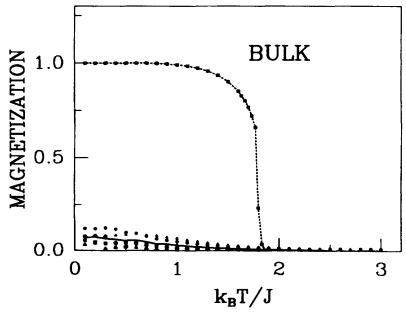

FIG. 2. The magnetization M plotted as a function of temperature. Five data sets are shown for $p = 0.5$ and one for the bulk ($p = 1$).

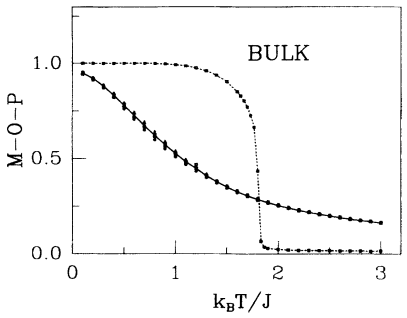

FIG. 3. Plot of MOP versus temperature. Five data sets are shown for $p = 0.5$ and one for the bulk ($p = 1$).

temperature becomes zero. (The percolation threshold, p_c, on a three-dimensional simple cubic lattice is ~ 0.307.) Indeed we find that $p_{\text{th}} < 0.5$. Our results were obtained with five independent runs on a $16 \times 16 \times 16$ lattice with $p = 0.5$ with 20 000 Monte Carlo passes used for obtaining averages and 5000 passes to reach equilibrium from a nearby temperature. The bulk results employed a $12 \times 12 \times 12$ lattice.

Figures 2–5 shows plots of M, MOP, SSCFP, and the specific heat as a function of temperature for $p = 0.5$ and $p = 0$ (the bulk case). Our results clearly indicate that even for $p = 0.5$, there is no long range order but sluggish dynamics as evidenced by the large MOP. Nevertheless, there is no evidence of hysteresis or history dependence for any of the quantities—independent runs carried out starting from different configurations led to practically identical results as did cycling the temperature. The behavior of MOP versus temperature strongly suggests that unlike the random-anisotropy Heisenberg ferromagnet [11] there is no evidence here of a transition to a spin glass phase. The results for the specific heat are in qualitative accord with experimental data [2]—furthermore, their dependence on the aerogel porosity (and hence p) has the same trend of recent experimental results [12]. As in the experiment, the specific heat peak sharpens, increases in magnitude, and moves towards the bulk peak as p is decreased.

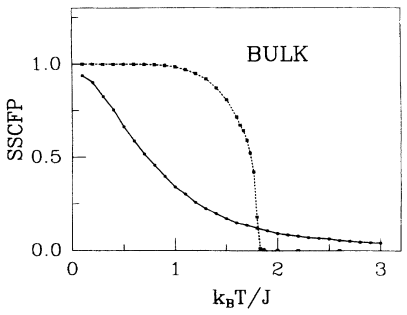

FIG. 4. Plot of SSCFP versus temperature. One data set each is shown for $p = 0.5$ and $p = 1.0$.

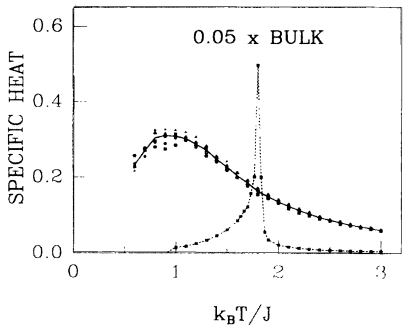

FIG. 5. Plot of specific heat versus temperature. Five data sets are shown for $p = 0.5$ and one for the bulk ($p = 1$). The bulk specific heat data have been scaled down by a factor of 20.

In summary, we have presented and analyzed simple models that are possibly capable of describing the isotropic-nematic transition in porous media or lack thereof. Even though our studies do not take into account the correlated geometry of the aerogel, they yield results in qualitative accord with existing experiments.

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Note added.—It would be interesting to determine whether the lower critical dimension of the random field Lebwohl-Lasher model is larger than three. We are indebted to Nihat Berker for suggesting this to us and for useful discussions.

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